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Magnetron Reactive Ion Etching of GaAs and AlGaAs in CH₄/H₂/Ar Plasmas

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| 13. ABSTRACT (Maximum 200 words) Magnetron reactive ion etching of GaAs and AlGaAs has been investigated in CH ₄ /H ₂ /Ar gas mixtures. Etch rate was determined as a function of gas composition, power density (0.4-1.0 W/cm ²), pressure (6-25 mTorr), and total flow rate (20-40 sccm). Hydrogen passivation effects of etched and rapid thermal annealed GaAs were studied for several anneal temperatures (300°C, 400°C). | | | | |
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INTRODUCTION

Reactive ion etching (RIE) is a plasma processing technique which has been widely used for etching III-V compound semiconductors such as GaAs and AlGaAs. Since the chlorides of Ga, Al, and As are relatively volatile, chlorine based chemistry is the logical choice for etching these materials. The corrosive and toxic characteristics of chlorine based gases make them difficult to handle, and although these problems can be minimized by using chlorofluorocarbons such as CCl_2F_2 (freon-12), these gases are being phased out because of environmental concerns.

CH_4/H_2 mixtures are an alternative choice for reactive ion etching III-V semiconductor materials. Some advantages of using these mixtures are that they are noncorrosive and nontoxic, prolonging the lifetime of the etch system and posing little hazard to the operator. These etch gas mixtures have been shown to provide controlled, smooth, anisotropic etching of GaAs and AlGaAs. The relatively low etch rates of these materials in CH_4/H_2 can be advantageous for applications requiring highly controlled, shallow etch depths, such as for HEMT gate recess etching. For applications requiring deeper etch depths and hence higher etch rates, such as for via hole etching, a number of workers^{1,2} have reported adding Ar to the CH_4/H_2 mixture to increase etch rates and reduce hydrocarbon deposits through the presence of this heavy, chemically inert species.

This technical report gives results for CH_4/H_2 etching of GaAs and AlGaAs using magnetron enhanced reactive ion etching (MIE), which is similar to RIE but with the addition of a magnetic field to confine the plasma electrons close to the wafer sample. This minimizes electron loss to the chamber walls and increases ionization efficiency, reactive species generation, and etch rates at lower operating pressures than for conventional (unmagnetized) RIE. Compared to RIE, the magnetic field of MIE allows a higher density plasma discharge to be created which can sustain itself at relatively low cathode bias voltages, resulting in low ion bombardment energies and therefore minimal etch-induced wafer damage.

DESCRIPTION OF EXPERIMENT

The etch experiments were performed in a MRC 710 magnetron reactive ion etch chamber having a powered cathode (13.56 MHz) containing two bar magnets, with two additional magnets located outside the chamber at the top of the chamber cover. The 1000 cm^2 area cathode is water cooled and covered with an aluminum pedestal which supports the wafer sample. Samples were thermally heat sunk to the cathode with high vacuum grease. The magnets provide a uniform magnetic field of 100 Gauss at the sample location. The chamber is typically evacuated to pressures in the 10^{-6} - 10^{-7} Torr range.

The GaAs samples used for etch rate measurements were Si-doped ($n=1.5\times 10^{18}/\text{cm}^3$) with a (100) surface orientation. The AlGaAs samples for etch rate measurements were obtained by molecular beam epitaxy (MBE) of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$ composition layers ($1\mu\text{m}$ thick, Si-doped, $n=2\times 10^{17}/\text{cm}^3$) onto (100) GaAs

substrates. For etch depth measurements the samples were patterned with AZ5214 photoresist and rinsed in $1\text{NH}_4\text{OH} : 10\text{H}_2\text{O}$ to remove native oxide from the semiconductor surface immediately prior to etching for 20 minutes. After etching, the photoresist was removed from the patterned samples by rinsing in acetone, and etch depth was measured using a Dektak profilometer. The gas mixture composition was adjusted by varying the amount of gas flow through the CH_4 , H_2 , and Ar flow meters. Etch rate was measured as a function of gas mixture composition, power density, pressure, and flow rate. The study of etch rates as a function of these various parameters provides valuable information in understanding the etch mechanisms.

The GaAs samples used for hydrogen passivation effect studies were $0.75\text{ }\mu\text{m}$ thick layers (Si-doped, $n=5\times 10^{16}/\text{cm}^3$) which were grown onto (100) GaAs surfaces. Depth profiles of the free carrier electron concentration were obtained from C-V measurements performed on a Polaron Semiconductor Profile Plotter. Post-etch annealing experiments were performed on a Heatpulse 410 rapid thermal annealer (RTA) in an $88\text{N}_2/12\text{H}_2$ environment.

ETCH RATE RESULTS

Figure 1 shows the measured etch rates for GaAs and AlGaAs as a function of the $\text{CH}_4/\text{H}_2/\text{Ar}$ etch gas mixture, indicated by the CH_4 percentage of the total flow rate. For these experiments, total flow rate was held constant at 30 sccm, Ar flow rate was constant at 10% of total flow rate (3.0 sccm), and the CH_4 and H_2 flow rates were varied. Power density and pressure were constant at $0.40\text{ W}/\text{cm}^2$ and 10 mTorr, respectively. GaAs etch rate increased as the CH_4 flow rate increased from 10% to about 35%, whereupon it decreased for further increases in CH_4 . The GaAs surface was residue free over this range of CH_4 values. Similarly, AlGaAs etch rate increased from CH_4 flow rates of 10% to 25%, and then decreased sharply when CH_4 reached 30%. The etch rate reduction for AlGaAs at 30% CH_4 was accompanied by the formation of a hydrocarbon deposit on the AlGaAs surface, which was not present at lower CH_4 flow rates where the higher H_2/CH_4 ratios prevented this formation.

The primary group III etch products for CH_4/H_2 etching of GaAs and AlGaAs are thought to be $(\text{CH}_3)_3\text{Ga}$ (trimethylgallium) and $(\text{CH}_3)_3\text{Al}$ (trimethylaluminum), although neither of these species has been directly observed. The group V etch product is most probably AsH_3 (arsine). The lower etch rate of AlGaAs compared with GaAs has been observed by others³ and is attributed to $(\text{CH}_3)_3\text{Al}$ having a much lower vapor pressure than $(\text{CH}_3)_3\text{Ga}$. The increase in CH_4 flow rate initially produces additional $(\text{CH}_3)_3$ species for reaction with the semiconductor surface, resulting in increased etch rates. For CH_4/H_2 etching there is always competition between etching and polymer deposition, with deposition eventually dominating and etch rate decreasing at higher CH_4 concentrations. Cheung et al.⁴ report that maximum GaAs etch rate in CH_4/H_2 occurs for approximately 15% CH_4 , while Figure 1 indicates a maximum GaAs MIE etch rate at about 30% CH_4 . This could be

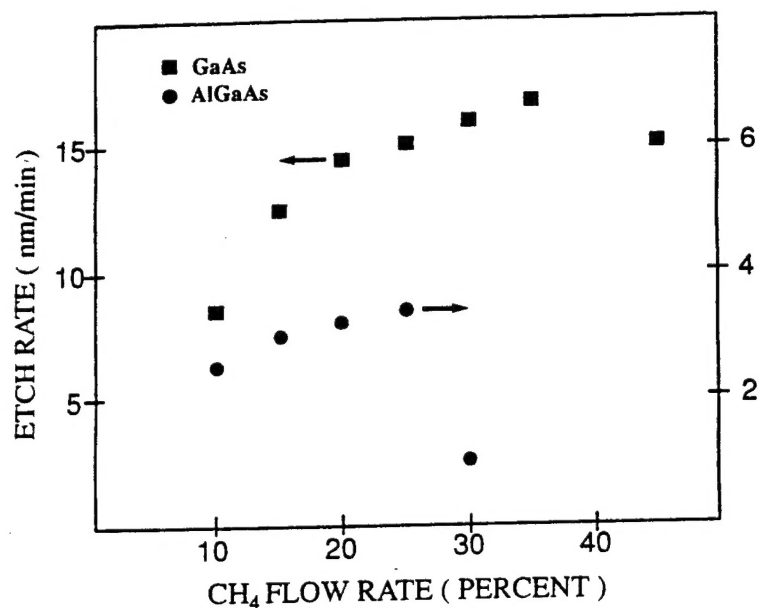


Figure 1. GaAs and AlGaAs etch rate in CH₄/H₂/Ar as a function of CH₄ percentage of total flow rate, with 30 sccm total flow rate, 3.0 sccm Ar flow rate, 0.4 W/cm² power density, and 10 mTorr pressure.

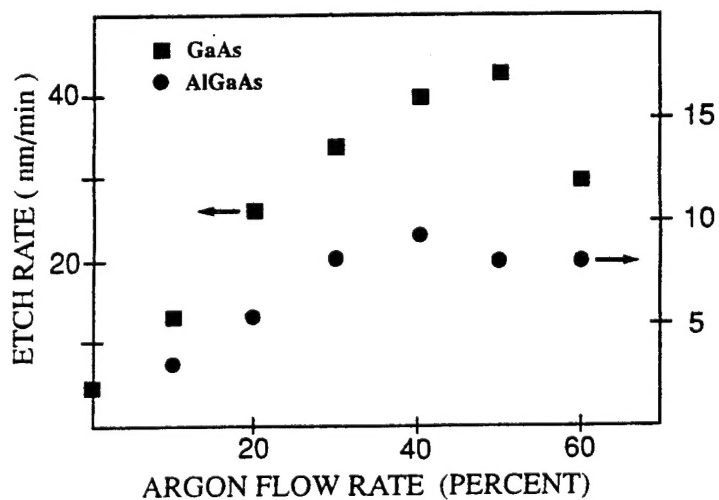


Figure 2. GaAs and AlGaAs etch rate in CH₄/H₂/Ar as a function of Ar percentage of total flow rate, with 30 sccm total flow rate, H₂/CH₄=5/1 flow rate ratio, 0.40 W/cm² power density, and 10 mTorr pressure.

due to the difference in plasma chemistries created by MIE compared to RIE, or possibly to the presence of Ar, which helps sputter the etch products from the surface and prevent polymer deposition at higher CH₄ concentrations. Since AlGaAs etch rates are less than for GaAs, AlGaAs etch rate peaks and polymer deposition dominates at lower CH₄ concentrations than for GaAs.

The dependence of etch rates on Ar flow rate over the range 0-60% of total flow rate is shown in Figure 2. For this data, H₂/CH₄ flow rate ratio was constant at 5/1, with 0.40 W/cm² power density, 10 mTorr pressure, and 30 sccm total flow rate. At 0% Ar, polymer deposition rather than etching took place for AlGaAs, and the GaAs etch rate was low (5 nm/min). For low Ar concentrations, etch rate increase with Ar flow rate was probably due to increased sputter removal of etch products. In this regime, etching is due to a combination of chemical reaction and physical sputtering at the semiconductor surface. As Ar concentration was further increased the etch rates peaked and eventually decreased at higher Ar concentrations where physical sputtering begins to dominate the etching process. A similar peak in etch rate was observed by Chaplart et al.⁵ for CCl₂F₂/Ar etching of GaAs.

The etch rate dependence on cathode power density is exhibited in Figure 3. As power density increases, the plasma density and associated concentration of reactive species also increases, resulting in higher etch rates. In addition, cathode self-bias voltage increased from 95 V to 150 V as power density increased from 0.4 W/cm² to 1.0 W/cm², resulting in higher ion bombardment energies and an enhanced sputtering effect. These cathode bias voltages are much lower than those reported by other workers for conventional RIE. For example, Law et al.⁶ reported a bias voltage of 600 V under conditions similar to those of Figure 3. Lower cathode bias voltages and ion bombardment energies lead to minimal etch-induced crystal damage for the MIE process, as has been shown for MIE of GaAs in CCl₂F₂.⁷ In spite of the lower bias voltages for MIE, the GaAs etch rates reported here are comparable to those reported by Law et al.⁶ for RIE under similar conditions.

The dependence of etch rates on pressure is shown in Figure 4, where etch rate increased with pressure over the range 5 to 25 mTorr. Cathode bias voltage also increased from 75 V to 130 V over this pressure range, resulting in an enhanced sputtering component of the etching at higher pressures. For reactant-limited etching, etch rate should increase as the pressure and hence the amount of reactant species supplied to the semiconductor surface increases. At higher pressures the etch rates show signs of saturation, particularly for AlGaAs. This may be an indication of increased gas-phase polymerization at higher pressures.

The relative independence of the GaAs and AlGaAs etch rates as a function of total gas flow rate over the range 20 - 40 sccm is shown in Figure 5. This indicates that the reaction chamber gas residence time, which is inversely proportional to flow rate, is longer than the surface reaction times for removal of the Ga, Al, and As etch products. The slight decrease in etch rates with increasing flow rate indicates that a minor portion of the etchant species is being pumped away before reaction with the semiconductor surface can take place, similar to the results reported by

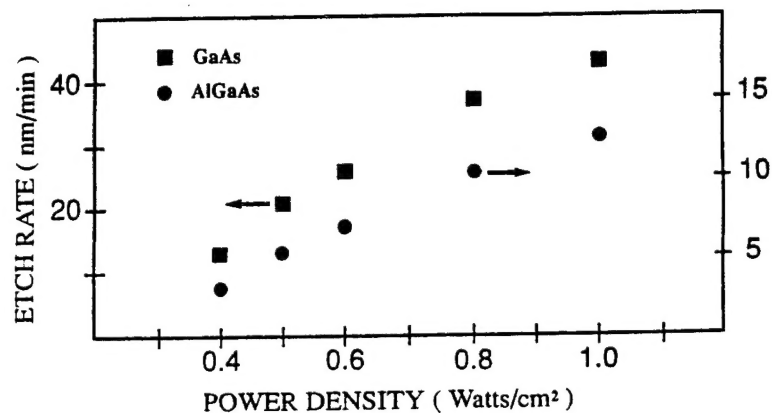


Figure 3. GaAs and AlGaAs etch rate as a function of power density, with 30 sccm total flow rate consisting of 4.5CH₄/22.5H₂/3.0Ar sccm flow rate mixture, and 10 mTorr pressure.

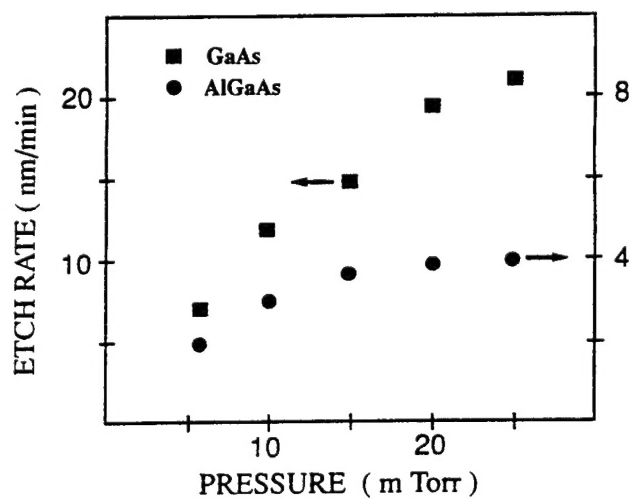


Figure 4. GaAs and AlGaAs etch rate as a function of pressure, with 30 sccm total flow rate consisting of 4.5CH₄/22.5H₂/3.0Ar sccm flow rate mixture, and 0.40 W/cm² power density.

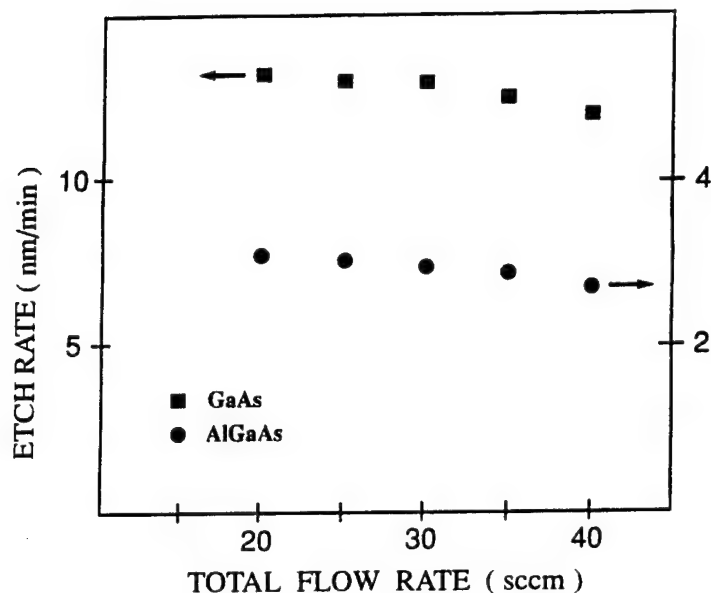


Figure 5. GaAs and AlGaAs etch rate as a function of total flow rate, with a $\text{CH}_4/\text{H}_2/\text{Ar}$ flow rate mixture of 1.5/7.5/1.0, 0.40 W/cm^2 power density, and 10 mTorr pressure.

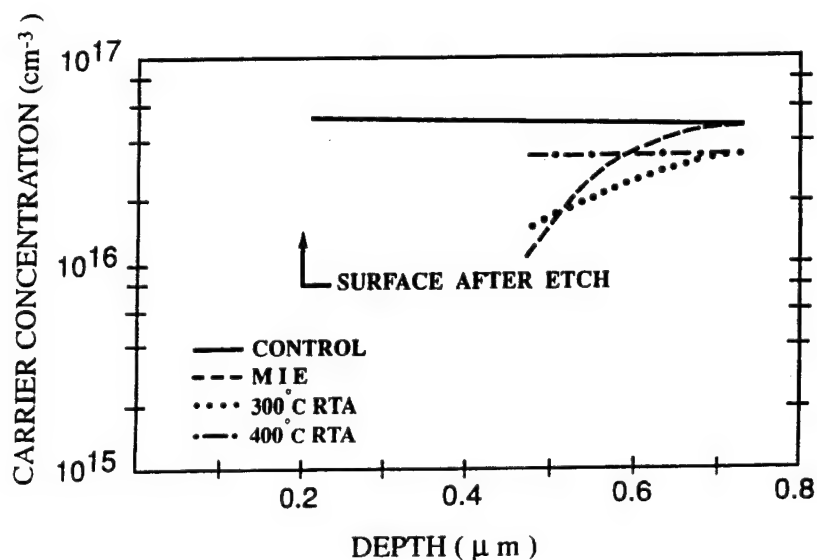


Figure 6. Free electron carrier concentration depth profiles in an MBE-grown GaAs layer ($0.75 \mu\text{m}$ thick) for control (unetched) sample, magnetron ion etched sample, and etched samples subsequently rapid thermal annealed at 300°C and 400°C for 30 sec.

Pearnton et al.⁸ for C_2H_6/H_2 RIE of InP and InGaAs. Cathode bias voltage was essentially constant at 100 V over the range of flow rates used.

HYDROGEN PASSIVATION

The creation of hydrogen atoms and ions in the plasma discharge and the subsequent diffusion of these species into III-V semiconductors is known to produce passivation of many types of donors and acceptors.^{9,10} For n-type Si-doped GaAs and AlGaAs, hydrogen is believed to bond to the Si donor, leaving it fourfold coordinated and electrically inactive. This results in a reduction of the surface region carrier concentration. Annealing samples etched in CH_4/H_2 has been found to be effective in reversing hydrogen passivation and restoring initial carrier concentrations. An effect similar to hydrogen passivation can be produced by bombarding ions from the discharge, which create surface region deep energy levels that trap conduction electrons and also reduce carrier concentration. This effect should be minimal for the MIE process because of its inherently low cathode bias voltages.

The hydrogen passivation effect was studied for MIE of GaAs in a $CH_4/H_2/Ar$ discharge. Figure 6 shows carrier concentration measurements performed on GaAs using Polaron C-V measurements. The control (unetched) sample carrier concentration was $5 \times 10^{16}/cm^3$. Etching to a depth of 0.2 μm in a 4.5 CH_4 /22.5 H_2 /3.0 Ar sccm flow rate mixture resulted in a reduction in the surface region carrier concentration. A subsequent rapid thermal anneal at 300°C for 30 sec redistributed the hydrogen, resulting in less passivation within about 0.3 μm of the etched surface and more passivation in the deeper region. An additional rapid thermal anneal at 400°C for 30 sec resulted in further restoration of the carrier concentration toward its initial value, but still left a residual hydrogen passivation effect. Higher temperatures may be required to completely remove all hydrogen passivation.^{11,12} Although surface passivation due to ion bombardment induced near-surface disorder and electron traps cannot be completely ruled out, the results reported here are consistent with passivation being due mostly to the presence of hydrogen. The results for the 300°C anneal are particularly characteristic of hydrogen diffusion effects.

SUMMARY

Magnetron reactive ion etch rates of GaAs and AlGaAs in $CH_4/H_2/Ar$ gas mixtures were found to increase with cathode power density and pressure, and were independent of gas flow rate. Increasing the Ar concentration results in higher etch rates until physical sputtering eventually begins to dominate the process at about 40-50% Ar concentration. GaAs etch rates were generally several times higher than AlGaAs etch rates. Most of the hydrogen passivation in GaAs could be reversed by rapid thermal annealing at 400°C for 30 sec.

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